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APPLICATION OF PATENT OF INVENTION

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(54) New fluorinated ethers and their preparation process.

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(71) Depositor: SOCIETE NATIONALE DES POUDRES ET EXPLOSIFS, residing in France.

(72) Invention of: Serge Lecoller, Daniel Boute and Olivier Reboul.

(73) Owner: Same as (71)

(74) Attorney:

The subject of the present invention is a new preparation process for fluorinated ethers and, as new industrial products, fluorinated ethers obtained with this process.

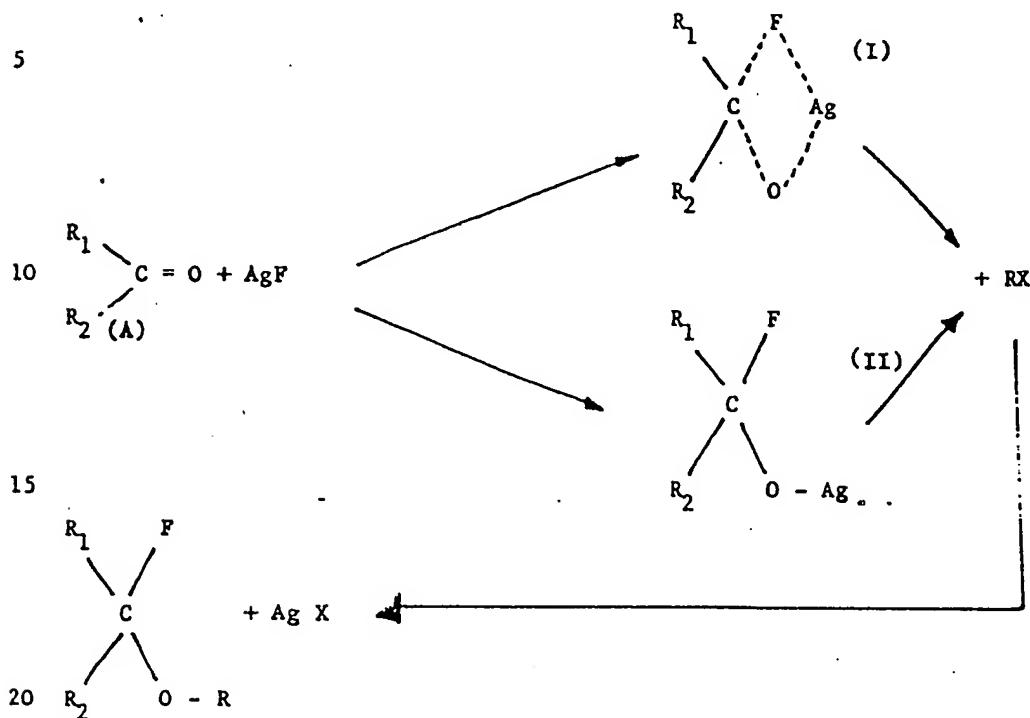
It is known by the English patent No. 1.153.187 and American patents Nos. 3.361.685, 3.504.000, 3.766.219 of PITTMAN and coll. and 3.549.711 of MERRILL and coll. for preparing fluorinated ethers from organic halogenides and organic perfluorinated compounds of alkaline metals.

PITTMAN and coll. describe glycide fluorinated ethers obtained by action of an epihalohydrine on fluorocarbonolate of alkaline metal. The reaction is done between 50 and 100°C, this range of temperature hurts the final product quality, reactive agents being not much stable at these temperatures. Yields are medium, about 70%. MERRILL and coll. describe fluorinated ethers obtained by action of an organic halogenide on perfluoroalcoholate of alkaline metal. Yields obtained are widely variable and the preparation must be operated under severe conditions of temperature and pressure. In the application for a French patent registered with the No. 73 - 46778, the applicant also describes certain fluorinated ethers obtained by action of an oxygenated complex of a perfluorinated silver with an organic halogenide.

However until now, no one has prepared fluorinated ethers of the type $R_f - CF_2 - O - R$ where R_f is a perfluorinated aliphatic chain and R an eventually substituted aliphatic radical. People do not know how to synthesize fluorinated ethers by action of an organic halogenide on silver perfluoroalcoholate or on an AgF - perfluoroketone complex, products in situ in an aprotic polar solvent, under ordinary conditions of temperature and pressure, with an excellent yield.

The process according to this invention consists, in a first phase, of producing a perfluorinated organic silver in solution by action of a perfluorocarbonyl compound on a suspension of silver fluoride in an aprotic polar solvent. Depending on whether said perfluorocarbonyl compound is a perfluoroketone or a fluoride of a perfluorinated acid, an AgF - perfluoroketone or a silver perfluoroalcoholate will be obtained. In a second

phase, the process consists of reacting said perfluorinated organic silver in solution, with an organic halogenide having the general formula RX, according to the following general reaction:



where R_1 is a perfluorinated alkylene chain, linear or branched, having 1 to 12 carbon atoms, where R_2 is, either the fluorine, at which case the perfluorocarbonyl compound (A) is a fluoride of perfluorinated acid and the product of its reaction on AgF is a silver perfluoroalcoholate (II), or a perfluorinated alkylene chain, linear or branched, having 1 to 12 carbon atoms, at which case the carbonyl compound (B) is a perfluoroketone and the product of its reaction on AgF is an AgF - perfluoroketone complex (I).

Naturally, without exiting from the framework of the process of this invention, compound (A) may be a perfluorodiacid fluoride. In the previous equation, RX designates an organic halogenide being able to comprise several X type atoms, identical or different, chosen from the group made up of chlorine, bromine and iodine, R being an alkylene or alkylarylene chain, linear or branched, capable of having functional groups chosen from those made up

with groupings of nitroso, nitro, sulfoxides, phosphine oxides, ethylene double liaisons, epoxy, chlorine, bromine, fluorine and iodine.

Advantage of the process according to this invention is this process is more accessible to the industry than previously known processes. In fact, operational conditions are less severe, yields are in general about 100%, there are no secondary reactions and the process application is not limited to only few organic halogenides: taken into consideration of the very high cost of fluorinated raw materials, the advantage offered by the characteristics of the process of this invention is much appreciated.

Detail on how to use the process according to this invention is described hereafter:

The process is done at ambient temperature in solvent medium. The choice of solvent is important and in general an aprotic polar solvent is chosen, solvent good for favoring reactions of the SN_2 type. The solvent is imperatively, rigorously anhydrous due to the very strong tendency to hydrolysis of silver perfluoroalcoholate or AgF - perfluoroketone complexes.

The process is operated in two phases. In the first phase, a preparation in situ of either the silver perfluoroalcoholate, or the AgF - perfluoroketone is done. Preparation of silver perfluoroalcoholate is the subject of a patent application jointly deposited with the present application and is done at ordinary temperature in an aprotic polar solvent by action of perfluoroacid fluoride on a suspension of silver fluoride in said solvent.

The solvent, the reactive agents, the equipment should be perfectly anhydrous and in addition the atmosphere inert.

Preparation of AgF - perfluoroketone complex is done under lightly different conditions. In a chamber, a partial vacuum is provided above a suspension of silver fluoride in an aprotic polar solvent freshly distilled, gas removed and dry and then the perfluoroketone is introduced. There is then in the chamber a perfluoroketone pressure lightly greater than the atmospheric pressure. Gas absorption by the suspension is done by contact with the liquid surface and is favored by agitation. The chamber is maintained at a temperature close to

0°C, heating may be detrimental to the complex which is not much stable. In general, absorption is over at the end of one hour. Disappearance of silver fluoride indicates the formation of a compound, which reveals, by its MNR spectrum of fluorine, to be an AgF - perfluoroketone complex and not a silver perfluoroalcoholate as in the case of perfluoroacid fluorides.

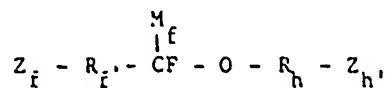
In a second phase, perfluorinated organic silver (AgF - perfluoroketone or silver perfluoroalcoholate) is allowed to react with an organic halogenide of the previously defined RX type. For this phase, it is not necessary to isolate the complex or the alcoholate which may be conserved in solution in said aprotic polar solvent. A stoichiometric amount of the organic halogenide, as defined in equations I or II, will be added to said complex or said alcoholate in solution. The addition is done without any particular precaution under normal ambient conditions of temperature and pressure, reactive agents remained, however, exempt from humidity. At the end of one-half hour, the reaction is over and fluorinated ether is isolated by distillation of the reaction product:

The yield is greater than 75% and in general, close to 100%. Fluorinated ether is characterized by its MNR spectrum of fluorine.

In general, it will be possible to use an aprotic polar solvent chosen, for example, from the group made up with hexamethyl phosphotriamide, dimethylsulfoxide, dimethylethers of ethyleneglycol, of diethyleneglycol, of triethyleneglycol, acetonitrile, N,N-dimethylformamide, the last two solvents being the preferred ones.

On the other hand, in certain cases the organic halogenide molecule lends itself with much difficulty to the previous elimination and less severe conditions should be used to accelerate the reaction speed: it will be possible, for instance, to heat the reaction mixture for 4 hours at 80°C, while conserving an important yield of pure product.

This invention also relates, as new industrial products, to fluorinated ethers having the following general formula:



where M_f is chosen from the group made up with

fluorine, at which case:

R_f is a perfluorinated alkylene chain, linear or branched, comprising 1 to 12 carbon atoms,
 R_h is an alkylene or alkylarylene chain, linear or branched, capable of having groupings
 nitro, epoxy, unsaturations and halogen atoms.

Z_h is chosen from the group made up with the grouping - O - R_h - Z_h at which case Z_h is
 a hydrogen atom, and the fluorine, at which case Z_h is a hydrogen atom or a group
 - O - CF_2 - R_f - F.

trifluoromethyl group, at which case:

R_f is a perfluoromethylene group.

R_h is a methylene group.

Z_f is a fluorine atom.

Z_h is chosen from the group made up with the radicals n-propyl, bromo-3, propyl and
 perfluoroisopropoxy-1 propyl.

The following examples are given as illustration of the process according to this invention
 and use various perfluorocarbonyl compounds.

Example 1: Synthesis of perfluoroisopropoxy-1 n-butene.

First, preparation of an AgF - perfluoroketone then said fluorinated ether.

In a 1 liter reactor containing a suspension of 12.7 grams (0.1 mole) of silver fluoride in
 200 ml of acetonitrile freshly distilled and gas removed, a partial vacuum of the container is
 made and 16.6 grams (0.1 mole) of perfluoroketone are introduced into the reactor.

Temperature of the reactor is maintained at 0°C and the mixture is stirred for 1 hour.

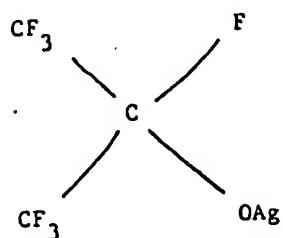
Obtained solution is lightly brown.

Obtained product is characterized by its MNR spectrum of fluorine, its acetonitrile solvent,
 its displacements calculated with regard to external trifluoroacetic acid (TFA):

singulet at 7.0 ppm

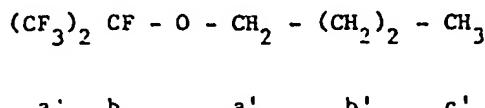
Therefore the compound is not a silver alcoholate:

but a $(CF_3)_2 CO$, AgF .



In a second phase, 13.7 grams (0.1 mole) of n-butyl bromide are added to the above obtained complex solution. The reaction is over at the end of one half hour at ambient temperature. Obtained fluorinated ether is isolated by distillation of the reaction product. 22 grams of perfluoroisopropoxy-1 n-butane are obtained, i.e. a yield of 91%.

This ether boils at 58°C and gives out the following MNR spectrums:



MNR spectrum ^1H : The operation is done in carbon tetrachloride, reference product being the trimethylsilane (TMS).

a': massif centered at 4 ppm

b': massif centered at 0.98 ppm and 1.9 ppm.

MNR spectrum ^{19}F : The operation is also done in carbon tetrachloride, external reference product being the trifluoroacetic acid (TFA).

a: massif centered at +4.0 ppm

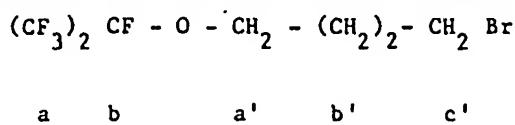
b: massif centered at +64.0 ppm.

Example 2: Synthesis of perfluoroisopropoxy-1 bromo-4 butane.

Organic silver complex is prepared as in example 1 then the complex is allowed to react with 0.1 mole of dibromo-1,4 n-butane. 30 grams of perfluoroisopropoxy-1 bromo-4 butane are obtained, i.e. a yield of 93%.

Obtained ether boils at 96°C and has the following MNR spectrums:

MNR spectrum ^1H : Solvent CCl_4 , reference product being the TMS.



a': massif centered at 4.03 ppm

b': massif centered at 1.82 ppm.

c': massif centered at 3.63 ppm.

MNR spectrum ^{19}F : Solvent CCl_4 , external reference product being the TFA

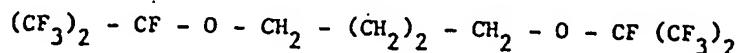
a: massif centered at +4.3 ppm,

b: massif centered at +64.5 ppm.

Example 3: Synthesis of diperfluoroisopropoxy-1,4 butane.

0.2 mole of organic silver complex in the example 1 is allowed to react with 0.1 mole of dibromo-1,4 butane. 38 grams of diperfluoroisopropoxy-1,4 butane are obtained, i.e. a yield of 89%. Obtained ether boils at 90°C and gives out the following MNR spectra:

MNR spectrum ^1H : Solvent CCl_4 , reference product being the TMS.



a b a' b' a' b a

a': massif centered at 4.12 ppm.

b': massif centered at 1.85 ppm.

MNR spectrum ^{19}F : Solvent CCl_4 , external reference product being the TFA.

a: massif centered at +4.0 ppm.

b: massif centered at +64.0 ppm.

Example 4: Synthesis of benzyloxy-1 n-perfluorooctane.

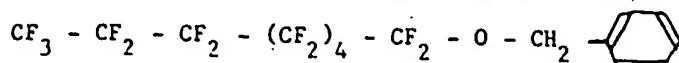
0.1 mole of silver perfluorooctanolate is prepared by reacting 0.1 mole of perfluorooctanoic fluoride with a suspension of 0.1 mole of silver fluoride in 500 ml of N,N -dimethylformamide, at 25°C in dry nitrogen atmosphere.

Then, 0.1 mole of benzyl bromide is added to the obtained alcoholate. The reaction is over at the end of one half hour and fluorinated ether is isolated by distillation.

47 grams of benzyloxy-1 n-perfluorooctane are obtained which boils at 120°C under 10 mm of mercury. The yield is therefore 90%.

Obtained ether is characterized by the following MNR spectra:

MNR spectrum ^1H : Solvent CCl_4 , reference product being the TMS.



a d e c b a' b'

a: singulet at 5.3 ppm.

b: singulet at 7.37 ppm.

MNR spectrum ^{19}F : Solvent CCl_4 , external reference product being the TFA.

a: massif centered at +5.05 ppm.

b: massif centered at +9.0 ppm.

c: massif centered at +44.0 ppm.

d: massif centered at +47.0 ppm.

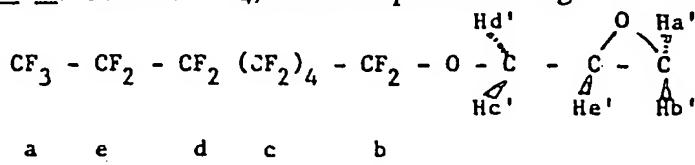
e: massif centered at +48.0 ppm.

Example 5: Synthesis of (epoxy-2,3 propoxy)-1 perfluorooctane.

0.1 mole of silver perfluorooctanolate is prepared as in example 4, then the alcoholate is allowed to react with 0.1 mole of bromo-1 epoxy-2,3 propane. The reaction mixture is heated at 80°C for 4 hours to accelerate the reaction speed.

41 grams of (epoxy-2,3 propoxy)-1 perfluorooctane are obtained, i.e. a yield of 80%. Obtained ether gives out the following MNR spectra:

MNR spectrum ^1H : Solvent CCl_4 , reference product being the TMS



a': quadruplet at 2.5 ppm.

b': triplet at 2.73 ppm.

c': multiplet at 3.08 ppm.

d' and e': massif at 3.97 ppm.

$$Ja' b' = 4.5 \text{ Hz} \quad Jc' b' = 4.5 \text{ Hz} \quad Je' a' = 2.5 \text{ Hz.}$$

MNR spectrum ^{19}F : Solvent CCl_4 , external reference product being the TFA.

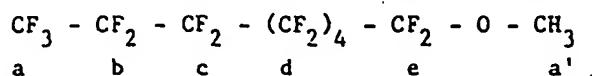
- a: massif centered at +5.5 ppm.
- b: massif centered at +9.75 ppm.
- c: massif centered at +41.1 ppm.
- d: massif centered at +44.0 ppm.
- e: massif centered at +45.0 ppm.

Example 6: Synthesis of methoxy-1 perfluorooctane.

0.1 mole of methyl iodide is allowed to react with 0.1 mole of silver perfluorooctanolate prepared as in example 4. 42 grams of methoxy-1 perfluorooctane are obtained, i.e. a yield of 93%.

Obtained ether gives out the following MNR spectra:

MNR spectrum ^1H : Solvent CCL_4 , reference product being the TMS.



a': singulet at 2.75 ppm.

MNR spectrum ^{19}F : Solvent CCl_4 , external reference product being the TFA.

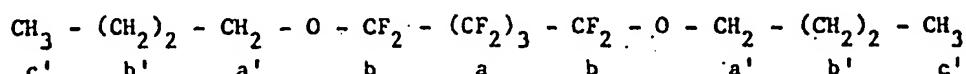
- a: massif centered at +7.7 ppm.
- b: massif centered at +45.8 ppm.

- c: massif centered at +46.8 ppm.
- d: massif centered at +42.5 ppm.
- e: massif centered at +14.2 ppm.

Example 7: Synthesis of dibutoxy-1,5 perfluoropentane.

0.1 mole of silver perfluoropentanediolate is prepared by reaction of 0.1 mole of fluoride of perfluoroglutaric acid with a suspension of 0.2 mole of silver fluoride in 1 liter of acetonitrile, at ambient temperature, in inert atmosphere. 0.2 mole of n-butyl bromide is added to the obtained silver solution. Then the solution is heated for 4 hours in solvent reflux. Obtained residue after evaporation of the solvent is distilled, and 30 grams of dibutoxy-1,5 perfluoropentane are obtained, i.e. a yield of 75%.

Obtained ether has the following formula:

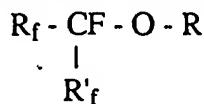


and gives out the following MNR spectrums:

MNR spectrum ^1H : Solvent CCl_4 , reference product being the TMS.

- a': triplet at 3.95 ppm.
- b', c': massif centered at 1.3 ppm. $\text{J}_{\text{a}' \text{ b}'} = 6 \text{ Hz.}$

Obtained fluorinated ethers in previous examples are new, and not only the large variety of organic halogenides in use but also fluorinated chains, shows the generality of the process of this invention. This invention brings therefore a considerable progress in the field of the above-mentioned fluorinated ethers, because, until today, people did not know how to prepare ethers having the formula $\text{R}_f - \text{CF}_2 - \text{O} - \text{R}$ and ethers having the formula



could not be obtained only in certain cases, under severe conditions and mediocre yields. Fluorinated ethers of this invention have notably an application as hypnotic and anesthetic agents, principally for those whose the boiling point is low, such as perfluoroisopropoxy-1 butane and an application as monomers useful for preparing heat-stable, fire-resistant or self-lubricant polymers such as (epoxy-2,3 propoxy)-1 perfluorooctane.

All these ethers, because of their properties, are also useful in phyto-sanitary and phyto-pharmaceutical fields.

C L A I M S

$$\begin{array}{c} M_f \\ | \end{array}$$

1) Fluorinated ethers having the general formula: $Z_f - R_f - CF - O - R_h - Z_h$

where M_f is chosen from the group made up with:

fluorine, at which case:

R_f is a perfluorinated alkylene chain, linear or branched, comprising 1 to 12 carbon atoms,
 R_h is an alkylene or alkylarylene chain, linear or branched, being able of having groupings
 nitro, epoxy, and halogen atoms.

Z_f is chosen from the group made up with grouping $- O - R_h - Z_h$, at which case Z_h is a
 hydrogen atom, and the fluorine, at which case, Z_h is a hydrogen atom.

trifluoromethyl group, at which case:

R_f is a perfluoromethylene group.

R_h is a methylene group.

Z_f is a fluorine atom.

Z_h is chosen from the group made up with n-propyl, bromo-3 propyl and
 perfluoroisopropoxy-1 propyl radicals.

2) Manufacturing process of fluorinated ethers having the general formula: $R_1 - CF - OR$

$$\begin{array}{c} | \\ R_2 \end{array}$$

where R_1 is a perfluorinated alkylene chain, linear or branched, having 1 to 12 carbon
 atoms, R_2 is chosen from the group made up with fluorine and a type R_1 chain, R is an
 alkylene or alkylarylene chain, linear or branched, being able of having groupings
 nitro-epoxy, unsaturations and halogen atoms, characterized by the fact that an organic
 halogenide comprising one or several halogen atoms chosen from the group made up
 with fluorine, chlorine, bromine, and iodine atoms, having the general formula RX
 where R the above-defined group, is allowed to react with a perfluorinated organic
 silver prepared by reaction of a suspension of silver fluoride with a perfluorocarbonyl
 compound chosen from the group made up with perfluoroketones and perfluoroacid
 fluorides, in an aprotic polar solvent, at temperature ranging between 10 and 80°C,
 under atmospheric atmosphere and rigorously anhydrous conditions.

- 3) Process according to claim 2, characterized by the fact that the perfluorinated organic ketones is prepared by reaction of the corresponding perfluoroketone with a suspension of silver fluoride, in an aprotic polar solvent, at ambient temperature, in inert atmosphere, under rigorously anhydrous conditions.
- 4) Process according to any one of claims 2 or 3, characterized by the fact that the aprotic polar solvent is chosen from the group made up with hexamethylphosphotriamide, N,N-dimethylformamide, dimethylsulfoxide, acetonitrile, dimethylethers of ethyleneglycol, of diethyleneglycol and of triethyleneglycol.

Translated by Henry D. Mai
Member of A.T.A.
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